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Thermodynamic functions of the three isomeric aminophenols

By V. N. Verma

Department of Spectroscopy, Banaras Hindu University
Varanasi-5, India

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Recently the author (1970) studied the vibrational spectra of the three isomeric aminophenols and made a complete assignment of the observed bands. With the help of the assignment of fundamental frequencies of these isomers, the thermodynamic functions have been calculated for an ideal gas for the three aminophenols at one atmosphere under the usual approximation of rigid rotator, harmonic oscillator model and the result is reported in the present communication.

The total energy ϵ of the system is given by the simple expression :

$$\epsilon = \epsilon_{trans}+\epsilon_{rot}+\epsilon_{vib}+\epsilon_{elec} \quad \ldots (1)$$

Where the subscript *trans* stands for translational, *rot*, for rotational, *vib* for vibrational and *elec* for electronic.

The partition function in terms of energy is given by

$$Q = \Sigma g_i e^{-\frac{\epsilon_i}{kT}} \quad \ldots (2)$$

Where g_i is the statistical weight, k is the Boltzmann constant and T is the absolute temperature.

Hence the total partition function (Q_t) is given by

$$Q_t = Q_{trans}+Q_{rot}+Q_{vib}+Q_{elec} \quad \ldots (3)$$

The electronic contribution is small and ignored because ϵ_{elec} is large compared to kT at ordinary temperature For the remaining partition functions, the standard expressions utilized by Colthup (1964) have been used and evaluated.

Considering the substituent groups as single mass point and the molecule a planar one, the principal moments of inertia I_x, I_y and I_z have been calculated, where y and z axes are in the plane of the molecule and the x axis is perpendicular to the plane. The structural data have been taken from the similar molecules such as phenol by Forest (1966), fluorophenol by Thakur (1968) and benzene by Allen *et al* (1950) because no microwave, electron diffraction or X-ray studies are available in the literature and so bond lengths and bond angles are not known exactly. The idea given by Sutton & Allen (1950) has also been taken into account that there is no appreciable change in the shape and size of the phenyl ring from its magnitude in benzene to benzene derivatives. With these assumptions the calculated moments of inertia for these three molecules are given in table 1.

TABLE 1. Moments of inertia in $10^{-40}g$ cm^2 for the three isomeric aminophenols

Moment of inertia (I)	*o*-Aminophenol	*m*-Animophenol	*p*-Aminophenol
I_x	687	687	697
I_y	295	295	145
I_z	392	392	552

Under the above assumption *o*- and *m*-aminophenols are classified into C_s symmetry with external symmetry 1 and *p*-aminophenol into C_{2v} symmetry with symmetry 2 as used by Herzberg (1945). The calculated values of the $C_v{}^0$ (heat capacity), $(H^0-E_0{}^0)/T$(enthalpy), $-(G^0-E_0{}^0)/T$ (free energy) and S^0 (entropy) at various temperatures ranging from 100-1500°K for the three isomers

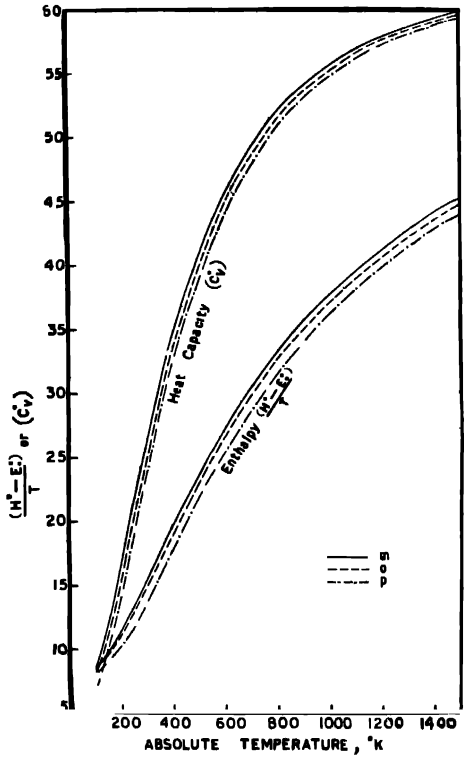

Figure 1. Variation of enthalpy and heat capacity with absolute temperatures for *o*- *m*- and *p*-aminophenol.

are represented by curves in figures 1 and 2 Here E_0^0 is the energy of one mole of an ideal gas at absolute zero, H^0 is its enthalpy, G^0 is its free energy.

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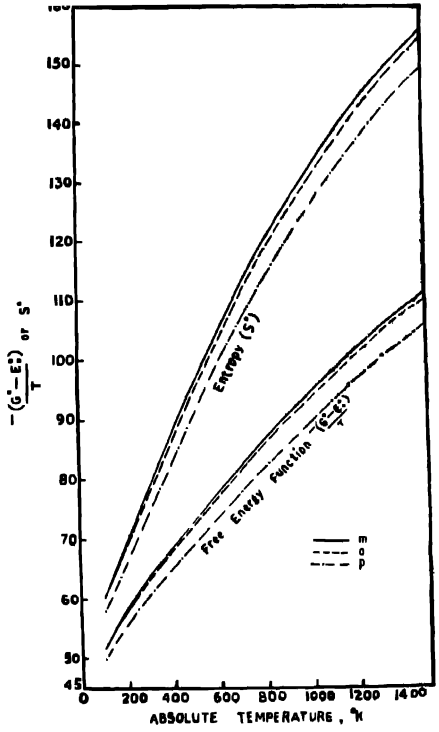

Figure 2. Variation of free energy function and entropy with absolute temperatures for *o*- *m*- and *p*-aminophenols.

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